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Technical Report No. 8

Complex Impedance, DSC and Lithium-7 NMR Studies of
Poly(propylene oxide) Complexed with $\text{Li}(\text{SO}_2\text{CF}_3)_2$
and with LiAsF_6

by

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Prepared for Publication in

Solid State Ionics

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94-17995

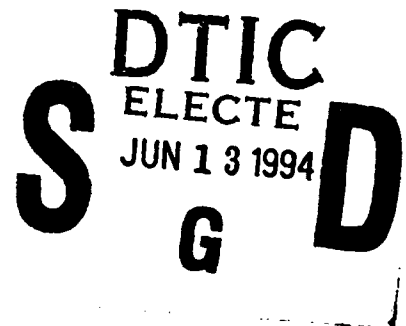


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REPORT DOCUMENTATION PAGE

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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 29 April 1994	3. REPORT TYPE AND DATES COVERED Interim Technical Report
4. TITLE AND SUBTITLE Complex Impedance, DSC and Lithium-7 NMR Studies of Poly(propylene Oxide) Complexed with LIN (SO ₂ CF ₃) ₂ , and with LiAsF ₆			5. FUNDING NUMBERS Grant # N00014-92-J-1629 R&T Code 4133037---01
6. AUTHOR(S) S. G. Brown, S. Greenbaum, M. G. McIn, M. C. Wintersgill and J. J. Fontanella			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Hunter College of CUNY, Dept. of Physics 695 Park Ave., New York, NY 10021			8. PERFORMING ORGANIZATION REPORT NUMBER 8
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research, Chemistry Division 800 N. Quincy Street, Arlington, VA 22217-5660			10. SPONSORING/MONITORING AGENCY REPORT NUMBER
11. SUPPLEMENTARY NOTES Accepted for publication in <u>Solid State Ionics</u> .			
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for pulic release; distribution unlimited.			12b. DISTRIBUTION CODE
13. ABSTRACT (Maximum 200 words)			

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14. SUBJECT TERMS Polymer Elctrolytes; Lithium-7 NMR Poly(propylene oxide)			15. NUMBER OF PAGES
			16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL

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Reprinted from

SOLID STATE IONICS

Solid state Ionics 67 (1994) 257-262
North-Holland

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Received 27 July 1993; accepted for publication 30 November 1993



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Complex impedance, DSC and lithium-7 NMR studies of poly(propylene oxide) complexed with $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ and with LiAsF_6

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Complex impedance/electrical conductivity, differential scanning calorimetry and ^7Li nuclear magnetic resonance measurements on poly(propylene oxide) complexed with two lithium salts $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ and LiAsF_6 , with compositions of eight ether oxygens per lithium, are reported. Ionic mobility, as probed by NMR linewidth and spin-lattice relaxation measurements, is strongly coupled to polymer segmental motion above T_g . The electrical conductivity for $\text{PPO}_8\text{LiAsF}_6$ is about an order of magnitude smaller than for $\text{PPO}_8\text{LiN}(\text{SO}_2\text{CF}_3)_2$. This is a consequence of the higher glass transition temperature for $\text{PPO}_8\text{LiAsF}_6$. The stretched exponential parameter β_{se} , obtained in fits to electric modulus data, was found to be about 0.51 for $\text{PPO}_8\text{LiN}(\text{SO}_2\text{CF}_3)_2$ and 0.57 for $\text{PPO}_8\text{LiAsF}_6$.

1. Introduction

Polymer electrolytes are currently the focus of much attention as potential electrolytes in lithium secondary batteries. The nature of the ion aggregation phenomenon in these materials remains the subject of great controversy. As a contribution to further understanding of this phenomenon a fundamental study of ion-polymer and ion-ion interactions in poly(propylene oxide) (PPO) complexed with two technologically important salts, lithium imide, $\text{LiN}(\text{SO}_2\text{CF}_3)_2$, and lithium hexafluoroarsenate, LiAsF_6 , has been undertaken. These salts are electrochemically very stable and have been extensively studied in liquid electrolytes, although much less so in solid polymer electrolytes.

Poly(propylene oxide) has been widely studied as a model system for fundamental studies of solvent-

free polymer electrolytes because it forms relatively homogeneous, non-crystalline polymer-salt complexes [1,2]. Nuclear magnetic resonance (NMR) measurements of cation nuclei, in particular ^7Li and ^{23}Na have been proven to be of value in probing cation-polyether and, in some cases, cation-anion interactions [3]. Further advances in understanding the ion transport mechanism and ion aggregation in PPO-salt complexes have resulted from analysis of complex impedance data either via traditional electrical conductivity or via the electric modulus representation [4]. In this study the ion-polymer and the ion-ion interactions of $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ and LiAsF_6 complexed with PPO are investigated via NMR measurements of the cation nuclei, differential scanning calorimetry (DSC), and electrical impedance measurements.

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2. Experimental

As in previously reported studies of PPO complexes [5], Parel-58 (Hercules, Inc.), which consists primarily (about 95 wt.%) of high molecular weight PPO, was employed as the host polymer. Appropriate mixtures, corresponding to a ratio of 1:8 Li:O, of PPO and lithium salt (imide salt obtained from 3M, and hexafluoroarsenate obtained from Lithco) were dissolved in acetonitrile (Alfa) and poured into shallow teflon dishes. Prior to use, the acetonitrile was distilled and the Li salts were dried under vacuum at 333 K for 48 h. Most of the solvent was removed by room temperature evaporation under partial vacuum (~ 20 mm) and the final preparation step consisted of heating the samples to 333 K under roughing vacuum for 72 h. Lower drying temperatures for longer periods are preferred for PPO complexes, which are known to exhibit salt-precipitation at higher temperatures [6]. A third sample for additional NMR measurements, $\text{PPO}_8\text{LiClO}_4$, was prepared in the same manner as the other two. Details concerning the DSC measurements, performed on TA Instruments Thermal Analysis console, are the same as described elsewhere for other materials [6]. ^7Li NMR relaxation and line width measurements were performed on a JEOL GX-400 NMR spectrometer according to procedures given in a previous paper [7]. Finally, the complex impedance measurements were carried out in a cell designed for liquids described in detail elsewhere [8]. The $\text{PPO}_8\text{LiN}(\text{SO}_2\text{CF}_3)_2$ sample was formed into the cell at about 423 K in a vacuum oven which had the secondary purpose of further drying the sample. The $\text{PPO}_8\text{LiAsF}_6$ sample was formed into the cell in situ at only 380 K since decomposition of the material was found to occur at higher temperatures. Each sample was subsequently transferred to the vacuum dewar where the electrical measurements were carried out.

3. Results and discussion

3.1. DSC

DSC thermograms (recorded at 10 K/min) for $\text{PPO}_8\text{LiN}(\text{SO}_2\text{CF}_3)_2$ and $\text{PPO}_8\text{LiAsF}_6$ are shown in

fig. 1 along with the results for the host material. It is apparent that the central glass transition temperature is about 259 K for $\text{PPO}_8\text{LiN}(\text{SO}_2\text{CF}_3)_2$ and about 291 K for $\text{PPO}_8\text{LiAsF}_6$. The latter T_g is typical of PPO-salt complexes with an 8:1 O:Li or O:Na ratio. For example, the central T_g in $\text{PPO}_8\text{LiClO}_4$ is 281 K [4]. For comparison, T_g in uncomplexed PPO is 213 K [5]. The elevation in T_g upon complex formation is a well known phenomenon in polymer electrolytes [1,2]. It is apparent from fig. 1 that some overshoot (an apparent endotherm) is observed just above the glass transitions of the polymer-salt complexes. This feature is commonly observed when the heating rate is different from previous cooling or heating rates that the material has experienced. Consequently, this feature is not considered further in the context of the present investigation. The $\text{PPO}_8\text{LiN}(\text{SO}_2\text{CF}_3)_2$ complex having a very low glass transition temperature is consistent with the well known "plasticizing" ability of the imide anion. Previously reported data on $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ -containing polymer electrolytes in the literature concern poly(ethylene oxide)-based electrolytes which are typically semi-crystalline complexes [9]. These $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ -poly(ethylene oxide) (PEO) complexes exhibited both higher amorphous contents and lower glass transition temperatures than analogous PEO-based materials containing the same concentration of other salts such as LiClO_4 . In the case of $\text{PPO}_8\text{LiN}(\text{SO}_2\text{CF}_3)_2$ the apparent "plasticizing" ability of the anion can be directly observed without

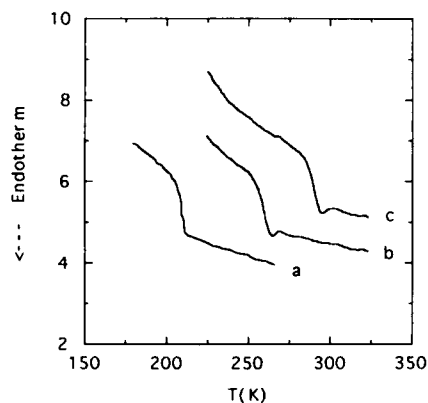


Fig. 1. DSC thermograms (scan rate 10 K/min) for: (a) uncomplexed PPO, (b) $\text{PPO}_8\text{LiN}(\text{SO}_2\text{CF}_3)_2$ and (c) $\text{PPO}_8\text{LiAsF}_6$.

the additional morphological effects observed in PEO complexes of the salt. For a fixed salt concentration, effects of changing the anion on T_g are commonly observed, if not always well understood. For example, PPO₈-salt complexes have T_g 's which vary from a minimum of 259 K in the present $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ sample to 306 K for a $\text{NaB}(\text{C}_6\text{H}_5)_4$ complex [4]. The idea of "transient crosslinking" of polyether segments by cations, which is invoked to explain the T_g elevation phenomenon referred to earlier [1,2], can be extended to anions when cation-anion interactions are significant. The low T_g of the PPO-imide material may be attributed to both the flexibility of the anion and the greater degree of ionic dissociation in the complex, relative to other salts. Reduced ionic association in imide relative to other lithium salts has been demonstrated in liquid electrolytes [10]. It is assumed that the imide salt retains this property in solid PPO complexes. Because ion pairing effects can contribute to structural rigidity in polymer electrolytes, it is reasoned that these effects contribute to the higher T_g 's of PPO complexed with other salts (besides the imide), along with the more rigid and symmetric structures of the other anions.

3.2. Complex impedance

The results of typical complex impedance measurements are shown in fig. 2. The bulk dc resistance was deduced from such plots and transformed to

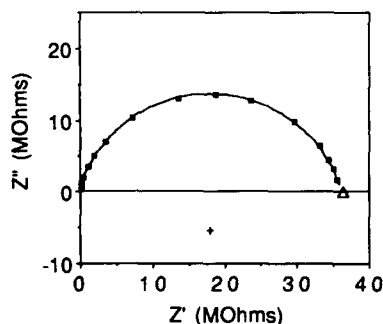


Fig. 2. Audio frequency complex impedance data for $\text{PPO}_8\text{LiN}(\text{SO}_2\text{CF}_3)_2$ at 275.1 K. The frequencies of the datum points from right to left begin at 10 Hz and increase in approximately equal logarithmic intervals with 4 frequencies per decade. The triangle represents the dc resistance and the plus sign designates the center of the Cole-Cole arc.

electrical conductivity using the appropriate geometrical factor for each sample. The resultant electrical conductivity as a function of temperature is shown by the squares in fig. 3 for $\text{PPO}_8\text{LiN}(\text{SO}_2\text{CF}_3)_2$ along with the apparent ac electrical conductivity, represented by the line segments. At high temperatures the dc conductivity is larger than the apparent ac conductivity because blocking electrode effects act to decrease the latter at the lowest frequencies. At low temperatures, the ac conductivity is larger than the dc conductivity because additional loss processes intrinsic to the material, such as dielectric relaxation (described in more detail later), begin to contribute to the apparent ac conductivity. The dc conductivity values extracted from the complex impedance analysis exhibit the expected VTF or WLF behavior [11–13] and were fitted by the equation:

$$\sigma = AT^{-1/2} \exp[-E_a/k(T-T_0)] \quad (1)$$

The data and best-fit VTF equation are replotted in fig. 4. The best fit parameters were found to be $T_0 = 213.7$ K, $E_a = 0.105$ eV, and $\log_{10}(A) = 1.04$ with an rms deviation in $\log_{10}(\sigma)$ of 0.0084. Consequently, T_0 is found to be 45 K below the central glass transition temperature, as determined by DSC. This is not unusual since $T_g - T_0$ is typically 40–50 K [6].

With the exception of much lower conductivity, the results for $\text{PPO}_8\text{LiAsF}_6$ are similar in appearance

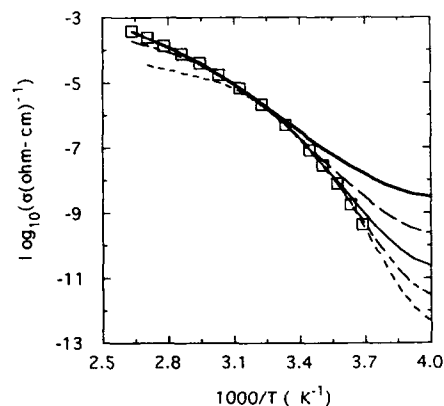


Fig. 3. Arrhenius plot for the electrical conductivity of $\text{PPO}_8\text{LiN}(\text{SO}_2\text{CF}_3)_2$. The lines are: short dash 10 Hz; chain link, 100 Hz; thin solid, 1000 Hz; long dash, 10000 Hz; thick solid, 100000 Hz. The squares are the dc conductivity as deduced from complex impedance analysis.

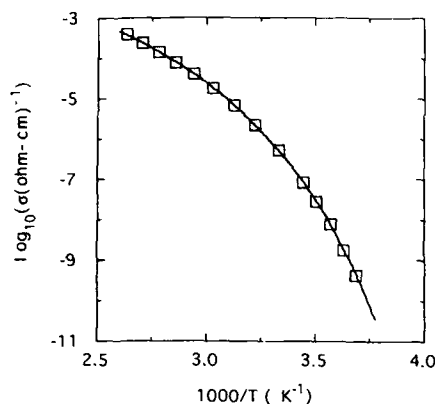


Fig. 4. Arrhenius plot for the dc conductivity obtained from complex impedance analysis for $\text{PPO}_8\text{LiN}(\text{SO}_2\text{CF}_3)_2$. The solid line is the best-fit VTF equation (eq. (1)).

to those for $\text{PPO}_8\text{LiN}(\text{SO}_2\text{CF}_3)_2$ and consequently are not plotted. The resultant best fit VTF parameters (eq. (1)) were found to be $T_0 = 231.5$ K, $E_a = 0.139$ eV, and $\log_{10}(A) = 1.56$ with an rms deviation in $\log_{10}(\sigma)$ of 0.012. Consequently, T_0 is found to be about 59 K below the central glass transition temperature, as determined by DSC. While this value is somewhat large, it is not unreasonable.

For completeness, the WLF equation:

$$\log_{10}[\sigma(T)/\sigma(T_g)] = [C_1(T - T_g)]/[C_2 + (T - T_g)] \quad (2)$$

and equivalent "standard" VTF equation:

$$\sigma = A' \exp[-E_a'/k(T - T_0')] \quad (3)$$

were also best-fit to the data. Using the central glass transition temperature of 259 K for $\text{PPO}_8\text{LiN}(\text{SO}_2\text{CF}_3)_2$, the WLF parameters in eq. (2) were found to be $C_1 = 11.5$, $C_2 = 44.4$, and $\log_{10}(\sigma(T_g)) = -11.8$. The "standard" VTF parameters were $T_0' = 214.6$ K, $E_a' = 0.101$ eV, and $\log_{10}(A') = -0.335$. The rms deviation is 0.0077. Using the central glass transition temperature of 291 K for $\text{PPO}_8\text{LiAsF}_6$, the WLF parameters in eq. (2) were found to be $C_1 = 11.6$, $C_2 = 58.8$, and $\log_{10}(\sigma(T_g)) = -11.5$. The "standard" VTF parameters were $T_0' = 232.2$ K, $E_a' = 0.136$ eV, and $\log_{10}(A') = 0.177$. The rms deviation is 0.012.

The impedance data were converted to electric modulus as described elsewhere [4]. Some of the

electric modulus results for the imide complex are shown in fig. 5 where they are plotted versus temperature. Data at thirteen other frequencies between 10 and 100000 Hz were also obtained. In fig. 5, two peaks are observed: a weak peak occurring at low temperatures, and strong peak occurring at higher temperatures. The weak peak is attributed to dielectric relaxation in the material. As discussed above, this relaxation is at least in part responsible for the difference between the dc and ac conductivities at low temperatures. This peak will not be considered further in the present paper. The strong peak, which occurs at higher temperature, is the conductivity relaxation. In order to characterize this peak further, the data were transformed into frequency plots such as that shown in fig. 6, where the electric modulus is plotted as a function of frequency at a fixed temperature (275 K). A stretched exponential [14] was best-fit to the central nine datum points as described elsewhere [4]. The stretched exponential parameter, β_{se} , was found to be about 0.51 for $\text{PPO}_8\text{LiN}(\text{SO}_2\text{CF}_3)_2$ and 0.57 for $\text{PPO}_8\text{LiAsF}_6$. Electric modulus plots obtained at other temperatures (not shown) yielded essentially the same β_{se} results. The value for $\text{PPO}_8\text{LiN}(\text{SO}_2\text{CF}_3)_2$ is close to the temperature-independent value of about 0.48 which was reported for seven of eight different salts in PPO [4]. The value for $\text{PPO}_8\text{LiAsF}_6$ is somewhat higher than expected.

The ionic conductivity mechanism in both the

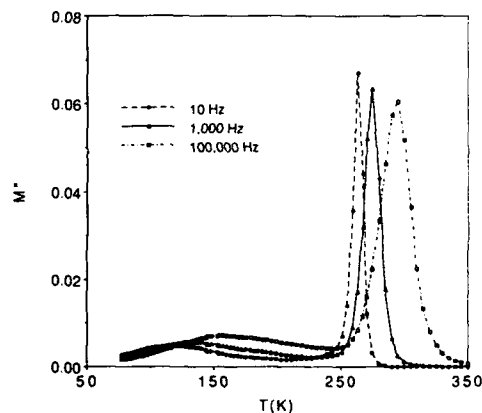


Fig. 5. Electric modulus versus temperature for $\text{PPO}_8\text{LiN}(\text{SO}_2\text{CF}_3)_2$. Straight line segments connect the datum points.

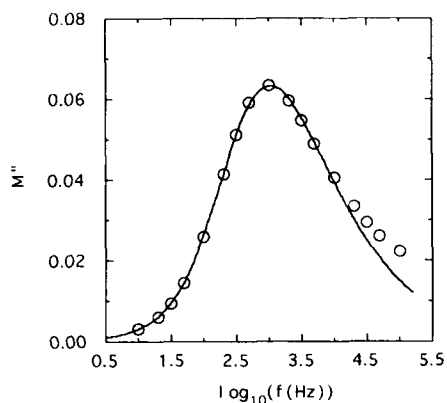


Fig. 6. Electric modulus versus frequency for $\text{PPO}_8\text{LiN}(\text{SO}_2\text{CF}_3)_2$ at 275.1 K. The solid line is the best-fit stretched exponential function.

LiAsF_6 and $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ PPO complexes appears to be unexceptional, compared to other amorphous polymer electrolytes, given the typical values for the best-fit β_{se} parameter for the conductivity relaxation in the imaginary part of the electric modulus and the observed values of $T_g - T_0$, as well as the observed VTF behavior of the ionic conductivity. The dc conductivity of the LiAsF_6 complex (not shown) is about an order of magnitude smaller than that of the $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ complex over the entire temperature range measured. Due to the similarities in their conductivity and modulus behaviors, the higher conductivity of the imide complex is attributed primarily to its lower T_g (and its correspondingly lower T_0). However an additional contribution to conductivity enhancement from reduced cation-anion interaction in the imide is also possible.

3.3. NMR

The ^7Li NMR spectrum of $\text{PPO}_8\text{LiN}(\text{SO}_2\text{CF}_3)_2$ at 218 K, well below T_g , is shown in fig. 7. The spectrum is characterized by ~ 20 kHz shoulders flanking a ~ 6 kHz (full width at half maximum) central line, the latter associated with the $\pm 1/2$ central transition while the shoulders correspond to a distribution of satellite transition ($\pm 3/2 \rightleftharpoons \pm 1/2$) frequencies. This distribution is attributable to the heterogeneous Li-polyether oxygen environment associated with the amorphous polymer complex. The

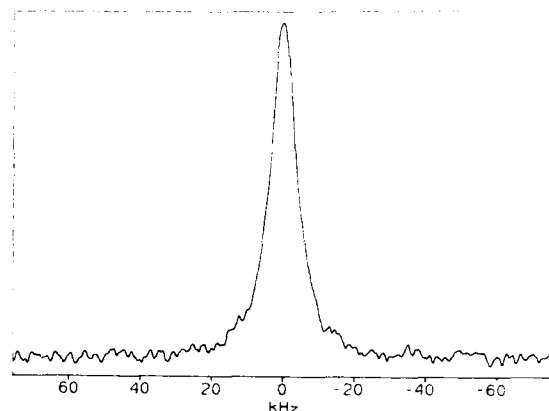


Fig. 7. ^7Li NMR spectrum of $\text{PPO}_8\text{LiN}(\text{SO}_2\text{CF}_3)_2$ at 218 K.

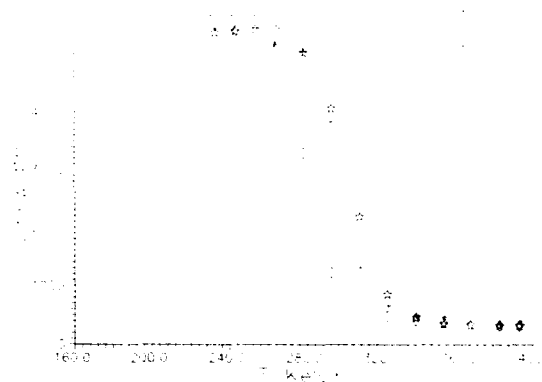


Fig. 8. Temperature dependence of the ^7Li NMR central transition linewidth in $\text{PPO}_8\text{LiClO}_4$ (+), $\text{PPO}_8\text{LiAsF}_6$ (★), and $\text{PPO}_8\text{LiN}(\text{SO}_2\text{CF}_3)_2$ (◇).

low temperature NMR spectrum is essentially unchanged until approximately T_g , at which point the satellite transitions vanish and the central transition begins to narrow. The temperature dependencies of the NMR central linewidths for the two polymer complexes (imide and hexafluororsenate) and a third sample, $\text{PPO}_8\text{LiClO}_4$ are displayed in fig. 8. The onset of motional line-narrowing of the imide complex clearly occurs at lower temperature than in the other two samples, in accord with the lower T_g of the first material. Motional narrowing is attributed to modulation of the $^7\text{Li}-^1\text{H}$ (the protons are, of course, in the polyether chain) magnetic dipole-dipole interaction resulting from polymer segmental motion above T_g . Similar results for Li salt-polyether com-

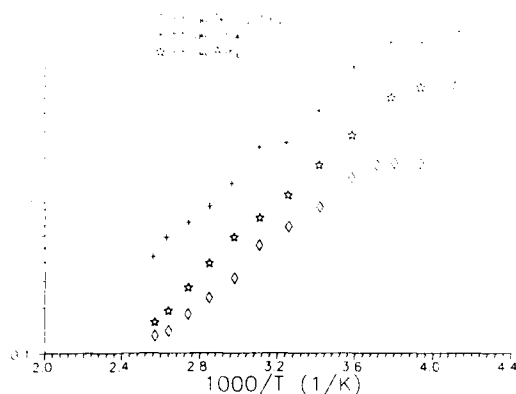


Fig. 9. Arrhenius plot of ^7Li spin-lattice relaxation times for $\text{PPO}_8\text{LiClO}_4$ (+), $\text{PPO}_8\text{LiAsF}_6$ (★), and $\text{PPO}_8\text{LiN}(\text{SO}_2\text{CF}_3)_2$ (◇).

plexes have been reported elsewhere [7,15]. Spin-lattice relaxation (T_1) data for the three PPO lithium salt complexes are presented in an Arrhenius plot in fig. 9. For all samples T_1 exhibits a monotonic decrease with increasing temperature, up to the highest observation temperature (390 K). It was not possible to observe the expected T_1 minima due to limitations of the variable-temperature NMR probe. The data do, however, convey the result that high frequency motions probed by the spin-lattice relaxation process are enhanced in the imide complex relative to the other two materials. That is T_1 , which is roughly proportional to the ionic motional correlation time at temperatures below the T_1 minimum [16], is lowest in the imide sample.

4. Conclusions

DSC and electrical studies of PPO_8LiX , where $\text{X}=\text{AsF}_6$ and $\text{N}(\text{SO}_2\text{CF}_3)_2$, show that the former material is quite similar to other PPO_8 -lithium salt complexes. The latter material exhibits an order of magnitude higher electrical conductivity, which is attributed to its significantly lower glass transition temperature. Electric modulus results, representative of the conductivity relaxation, for both materials are well described by a stretched exponential

decay function, as found for other PPO-salt complexes [4]. Li^+ ion dynamics as probed by NMR line-narrowing and spin-lattice relaxation (T_1) indicate that the lower T_g of the imide complex is manifested by a lower temperature onset of line-narrowing as well as a shorter T_1 , relative to the other samples.

Acknowledgement

This work was supported in part by the Office of Naval Research.

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